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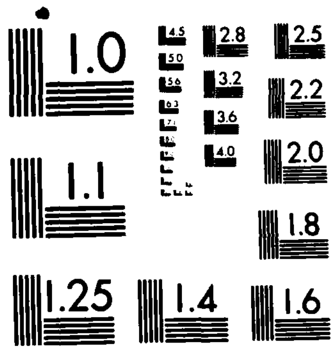

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SPECIATION OF BUTYLTINS AND METHYLTINS IN SEAWATER AND MARINE SEDIMENTS BY HYDRIDE DERIVATIZATION AND ATOMIC ABSORPTION DETECTION

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A sensitive and selective speciation method for direct determination of butyltins in seawater and marine sediments has been developed from published methods previously discussed in scientific literature. Monobutyltin, dibutyltin, and tributyltin may be detected in natural seawater samples at concentrations below 0.01 µg/liter. Sample stability during frozen storage in polycarbonate plastic containers was evaluated and found to be consistent over a 100-day storage period. Analysis of seawater samples by standard additions has compared well with butyltin concentrations, determined by calibration curve calculations in samples collected from open harbor sites. Less agreement between standard addition and calibration curve calculation of butyltin concentrations was seen when marine sediments were analyzed by direct borohydride derivatization. Greater problems with sample homogeneity and potential matrix interferences from high hydrocarbon and sulfide concentrations complicate marine sediment analysis. Some form of a sample pretreatment may be necessary to better determine butyltin concentrations in complex marine sediments.

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SUMMARY

A sensitive and selective speciation method for direct determination of butyltins in seawater and marine sediments has been developed from published methods previously discussed in scientific literature. Volatile butyltin hydrides are formed by sodium borohydride derivatization and detected by atomic absorption at a tin-selective wavelength of 286.3 nm.

Monobutyltin, dibutyltin, and tributyltin may be detected in natural seawater samples at concentrations below 0.01 μg/liter. The relative precision of the method defined as the coefficient of variation (standard deviation divided by the mean) generally lies within the range of 5 to 20 percent at butyltin concentrations near 0.01 μg/liter. A mean value of 92.6-percent recovery was achieved with several concentrations of tributyltin standards added to seawater. An interlaboratory comparison with the National Bureau of Standards has demonstrated a high degree of accuracy and precision.

Sample stability during frozen storage in polycarbonate plastic containers was evaluated and found to be consistent over a 100-day storage period. No loss of tributyltin was observed. Additionally, no monobutyltin or dibutyltin degradation products were detected.

In the analysis of complex environmental samples, some analytical interferences may be encountered. This is particularly true where fuel oils are present at high concentrations. Analysis of seawater samples by standard additions has compared well with butyltin concentrations, determined by calibration curve calculations in samples collected from open harbor sites. Less agreement between standard addition and calibration curve calculation of butyltin concentrations was seen when marine sediments were analyzed by direct borohydride derivatization. Greater problems with sample homogeneity and potential matrix interferences from high hydrocarbon and sulfide concentrations complicate marine sediment analysis. Some form of a sample pretreatment may be necessary to better determine butyltin concentrations in complex marine sediments.

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BACKGROUND

The U.S. Navy has made the decision to implement tributyltin containing antifouling coatings into the Fleet based on environmental documentation that has been completed and approved (Federal Register Vol. 50, No. 120, 21 Jun 85) in accordance with the National Environmental Policy Act. This decision is based on a critical need to substantially reduce the amount of propulsion fuel used by the Fleet and the frequency of overhaul periods and to increase operational capabilities.

To evaluate the environmental ramifications of the Fleet use of organotin containing coatings, from both drydock discharges and the leaching of tributyltin from hulls, a trace level speciation technique needed to be optimized and validated. The ability to measure subparts per billion tributyltin and its degradation products reliably, in water and sediment, is a critical requirement to determine the fate and effects of this compound in the marine environment as well as to monitor environmental levels prior to and during Fleet implementation. This report discusses an optimized technique for trace butyltin speciation in seawater and sediments.

TABLES

INTRODUCTION

Recently, butyltins have been detected in environmental samples that were acquired in areas where input from antifouling paints was probable by various analytical methods (Maguire et al., 1982; Seidel et al., 1980; and Waldock & Miller, 1983). Among these, the derivatization of inorganic tin, methyltin, and butyltin species to their respective volatile hydride forms by reduction with sodium borohydride has been successfully employed by several investigators in analysis of environmental samples (Braman & Tompkins, 1979; Hodge et al., 1979; Jackson et al., 1982; Seidel et al., 1980; and Tugrul et al., 1983). Sodium borohydride derivatization is not selective for tin II or tin IV. Both species are reduced to the tin IV form (Maguire et al., 1982).

The borohydride derivatization method has been reviewed with respect to potential analytical interferences (Andreae, 1981). Use of an atomic absorption detector may avoid problems encountered with the presence of water, CO_2, or H_2S. Loss of significant fractions of hydrides to the internal walls of the analytical apparatus by irreversible absorption was noted as the most persistent difficulty encountered in ultratrace analysis of organotins when using the hydride derivatization method (Andreae, 1981).

The presence of tributyltin has not been reported in marine environmental samples by hydride derivatization. Based on successful documented results with the method in determination of organotins, particularly with butyltins, we believed a sensitive speciation method for the determination of tributyltin, dibutyltin, and monobutyltin in marine environmental samples could be developed employing the hydride derivatization method. This report is a summary of our method development results.

METHODS AND MATERIALS

The hydride derivatization method (HDAA) of producing volatile tin species for detection by modified hydrogen flame atomic absorption spectrophotometry used in this study was a synthesis of methods described by Braman and Tompkins (1983) and Hodge, et al. (1979). Inorganic and organotin compounds in seawater are derivatized to inorganic and the respective alkyltin hydrides by $NaBH_4$ before detection. Briefly, a sample is placed into a 500-ml gas washing bottle, and acetic acid (2N) is added to lower the solution pH to 5.0-5.5. The sample is purged for 5 minutes with helium to remove oxygen prior to the addition of 4-percent $NaBH_4$ in 1-percent NaOH. The tin hydrides are purged and trapped in a glass U-tube (2mmID) that has been packed with quartz wool or 3-percent OV1 Chromosorb. The U-tube is immersed in liquid nitrogen to a level just above the packing material during the purge and trap cycle. The sample is purged for 5 minutes after addition of $NaBH_4$ to insure the maximum removal of tin hydrides from the solution. The trap is then removed from the liquid nitrogen bath, and tin species are detected sequentially, according to their boiling points, as they volatilize from the trap into the carrier gas. Normally, in the absence of other alkyltins, the first three tin species to volatilize from the trap as it comes to room temperature are SnH_4, butyltin trihydride ($BuSnH_3$), and dibutyltin dihydride (Bu_2SnH_2).

These species are carried into a quartz burner and are detected by an atomic absorption spectrophotometer (Buck Instruments, GBC SB9000). Dibutyltin detection may be improved by placing the trap in a 50 °C water bath. This causes a more rapid release of the dibutyltin hydride and results in a significantly sharper peak. Gas flow rates are 220/140/40 ml per minute with respect to hydrogen, air, and helium. The analytical wavelength is set at 286.3 nm. The HDAA system is shown in Figure 1.

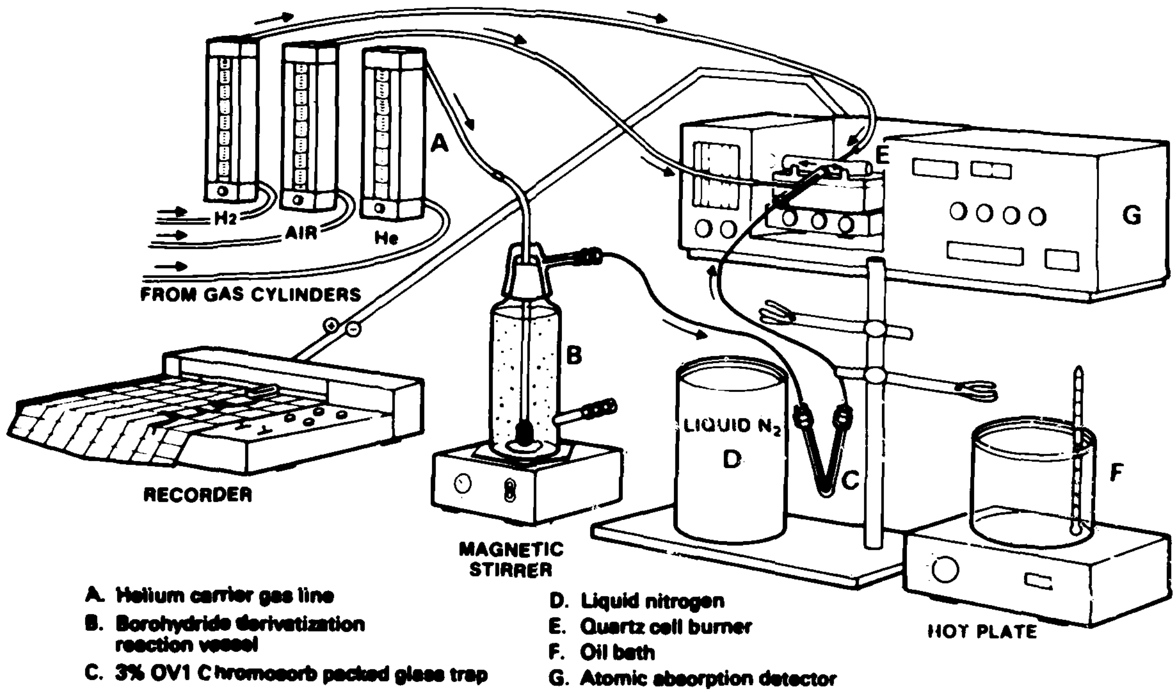


Figure 1. Hydride generation/atomic absorption spectrophotometry system for measurement of organotin species.

Volatilization of tributyltin hydride (Bu_3SnH) requires heating the trap in an oil bath at 140 °C. Lesser temperatures are possible. However, temperatures of 140 °C or higher result in better peak resolution. Standardization is accomplished by the addition of the appropriate alkyltin standard (in EtOH carrier) to the unknown or by calibration with standard curves. Calculations are based on peak area integration. The detection limit for inorganic tin hydride is 0.001 µg/liter. Mono-, di-, and tributyltin hydrides may be detected at 0.006, 0.009, and 0.007 µg/liter, respectively. The amount of Chromosorb used in the trap and the number of samples processed may cause small variations in detection limits.

Earlier studies were conducted with quartz wool column packings. Subsequent experiments demonstrated that 3-percent OV1 Chromosorb was a superior packing material. U-traps packed with 3-percent OV1 Chromosorb (approximately 1 gm per trap) exhibited sharper, more clearly resolved peaks than those produced with quartz wool. The better peak resolution achieved with Chromosorb packing is of particular significance when samples containing butyltins at near-detection limits are analyzed. A detailed description of the HDAA method including required materials is given in Appendix A.

RESULTS AND DISCUSSION

A. Precision Data

The relative precision of the hydride derivatization method, expressed as the coefficient of variation (standard deviation divided by the mean of N measurements), was determined for inorganic tin in seawater. An inorganic tin standard was prepared from a 1000-mg/liter atomic absorption standard by dilution in 1-percent HCl/deionized water. Aliquots were withdrawn from this working tin standard and analyzed at a concentration of 0.04 μg/liter. The results of four replicate analyses of a standard solution gave a mean absorbance of 0.073 with a standard deviation of 0.015 absorbance units. The coefficient of variation was 20.5 percent. The absorbance values for individual determinations were 0.068, 0.051, 0.085, and 0.087.

Further studies were initiated to determine the relative precision of the hydride derivatization method for detection of tributyltin, as well as dibutyltin and monobutyltin hydride species, in a seawater matrix at environmental concentrations characteristic of those recently reported (Maguire et al., 1982). Monobutyltin, dibutyltin, and tributyltin standards were prepared in a seawater matrix at a concentration of 0.036, 0.028, and 0.030 μg/liter, respectively. All three butyltin species were analyzed in the same reaction solution concurrently. Tin-selective analytical wavelengths of 286.3- and 224.6-nm were used to detect the hydride species formed. The 224.6-nm wavelength is more energetic and sensitive for tin detection; however, more signal noise is present. Therefore, we routinely use the 286.3-nm wavelength for tin-selective detection. The results of analysis of the three butyltin species at environmental concentrations are presented in Table 1.

Table 1. Relative analytical precision of monobutyltin, dibutyltin, and tributyltin chloride standards in seawater.

		Absorbance (In^2)		
		Monobutyltin 0.036 μg/l	Dibutyltin 0.028 μg/l	Tributyltin 0.03 μg/l
286.3 nm		0.095	0.062	0.032
		0.134	0.078	0.030
		0.093	0.064	0.025
	CV=	17.8%	10.3%	10.3%
		0.222	0.161	0.083
224.6 nm		0.121	0.123	0.075
		0.123	0.139	0.085
	CV=	30.3%	11.3%	4.9%

An additional group of butyltin standards was prepared at concentrations approaching the detection limit (0.005 μg/liter) for the three butyltin species. The results of repetitive analysis of this second group of butyltin standards are presented in Table 2.

Table 2. Repetitive analysis of butyltin chloride standards in seawater at environmental concentrations.

Butyltin Species	Number of Analysis	Mean Peak Area (In^2)	Standard Deviation	Coefficient of Variation
Monobutyltin 0.017 μg/liter	5	0.025	0.003	12.0%
Dibutyltin 0.019 μg/liter	5	0.041	0.007	17.1%
Tributyltin 0.014 μg/liter	5	0.016	0.001	6.3%

To assess analytical variability in the detection of tributyltin in environmental samples at sub-ppb concentrations, triplicate analyses were performed on San Diego Bay marine water samples collected during December 1984. Samples were collected in a 24-liter polycarbonate bottle and poured into three 1-liter polycarbonate bottles. Each bottle was then analyzed once as one of three determinations. The results of the triplicate analyses of environmental water samples are presented in Table 3 as tributyltin chloride.

Table 3. Hydride derivatization and atomic absorption detection of tributyltin (μg/liter) in marine water samples from San Diego Bay.

Sample	Mean Tributyltin Concentration	Standard Deviation	Coefficient of Variation
SD-3-38F	0.095	0.009	9.5%
SD-3-38H	0.093	0.020	21.5%
SD-3-38I	0.073	0.017	23.3%
SD-3-38E	0.021	0.001	4.8%
SD-3-38G	0.019	0.006	31.6%
SD-3-38D	0.009	0.002	22.2%
SD-3-18	0.018	0.002	11.1%

Analysis of butyltin standards in seawater at environmental concentrations indicate that the relative precision of the hydride derivatization method is reasonably consistent among butyltin species at both tin-selective analytical wavelengths. Additionally, the analytical variability determined by repetitive analysis of butyltin standards and environmental marine water samples at sub-ppb concentrations is comparable. The percent variation in the amount of butyltin detected at such low concentrations in standards and environmental samples is small.

B. Intercalibration

1. **Comparison of Hydride Derivatization and Graphite Furnace Atomic Absorption Determinations of Butyltin in Seawater and Deionized Water.** To assess the relative accuracy of the hydride derivatization method for determination of butyltin in seawater, we compared analytical results with another analytical method developed at the Naval Ocean Systems Center (Dooley & Homer, 1983; Homer & Dooley, 1983). Although the graphite furnace atomic absorption (GFAA) method for analysis of butyltin in seawater is not a speciation method, this condition is not restrictive if tributyltin is the only butyltin species present in solution. Organic solvent extraction with methyl isobutylketone followed by graphite furnace atomic absorption detection has demonstrated quantitative (97 percent) recovery of tributyltin from seawater (Homer & Dooley, 1983).

Solutions of tributyltin in seawater were made from primary standards prepared in 95-percent EtOH. Both tributyltin chloride (TBTCl) and bis(tri-n-butyltin) oxide (TBTO) (from commercial sources) were used to prepare the unknown seawater samples without further purification. The results of analysis of the unknown seawater samples by hydride derivatization and graphite furnace atomic absorption methods are presented in Table 4. Theoretical concentrations and analytical results are expressed as inorganic tin (Sn) in μg/liter.

Table 4. Determination of tributyltin in seawater by HDAA and GFAA analysis.

Sample Number	HDAA	Percent R	GFAA	Percent R	Theoretical Concentration μg/liter
1	34.9	98.0	40.8	114.6	35.6 (TBTCl)
2	32.6	96.4	37.6	111.2	33.8 (TBTO)
3	21.0	78.7	24.0	89.9	26.7 (TBTCl)
4	11.6	68.6	12.0	71.0	16.9 (TBTO)
5	10.8	121.3	7.3	82.0	8.9 (TBTCl)
		$\bar{X}$=92.6 percent		$\bar{X}$=93.7 percent	

Percent recovery of the theoretical concentration of tributyltin in seawater expressed in μg/liter Sn ranged from 68.6 to 121.3 percent by the HDAA method. Percent recovery by the GFAA method ranged from 71.0 to 114.6 percent. Mean recoveries were 92.6 and 93.7 percent for the HDAA and GFAA methods, respectively. These similarities in analytical results indicate that both methods are capable of accurate determination of tributyltin in a seawater matrix.

Recently, an interlaboratory comparison of organotin measurement methods was initiated by the United States National Bureau of Standards (NBS). Our laboratory participated in this exercise and provided analytical results for an unknown tributyltin sample in deionized water by HDAA and GFAA analysis. The results of the overall laboratory comparison are not yet available.

However, the results by HDAA and GFAA analysis of replicate aliquots of the unknown sample given our laboratory were in close agreement. These data are presented in Table 5 as mg/liter tributyltin chloride. Values reported for HDAA and GFAA analysis represent individual determinations of separate sample aliquots.

Table 5. Comparsion of HDAA and GFAA analysis of tributyltin in deionized water (mg/liter TBTCl).

HDAA	GFAA
2.92	3.03
2.92	2.36
2.58	2.49
2.92	2.23
2.58	2.78
2.99	2.36
3.09	2.23
2.67	2.36
$\overline{X}$=2.83; STDV=0.20	$\overline{X}$=2.48; STDV=0.28
S/$\overline{X}$=7.1 percent	S/$\overline{X}$=11.3 percent

The results of HDAA and GFAA analysis of tributyltin in a deionized water matrix compare well, indicating that both methods detected the same amount of analyte in repetitive analysis of the unknown tributyltin solution. To date, NBS has not formally released information regarding the actual concentration of tributyltin in solution. However, we have been informed that the measured amount of tin in the unknown sample was 1.06 ppm $\pm$0.44 percent (W. Blair, NBS, telephone conversation, April 1985). This value corresponds to 2.90 ppm as TBTCl using a molecular weight correction factor of 2.74. Both results by HDAA and GFAA methods are in close agreement with this value, 97.6 percent and 85.5 percent recovery, respectively. Previous comparisons with the HDAA and GFAA methods in seawater solutions (Table 4) indicate that both methods are accurate in a seawater matrix. The data generated in deionized water suggest that both methods may be accurate in this matrix, as well.

C. Frozen Sample Storage

Numerous reports have appeared addressing the presence of butyltins in environmental samples. However, little information exists regarding sampling procedures and storage conditions. Polyethylene plastic containers have been shown to absorb 62 percent of the initial TBTO in seawater solution after a 1-week period at 4 °C. Polycarbonate plastic and Pyrex glass containers exhibited much smaller adsorption losses over the same period (3 and 4 percent, respectively), while Teflon containers adsorbed 7 percent of the TBTO initially present (Dooley & Homer, 1983). Dibutyltin is used as a stabilizer in the manufacturing of many plastics and has been shown to leach from polyvinylchloride pipe (Boettner et al., 1982). Clearly some forethought must be given to the selection of appropriate sampling containers to avoid serious adsorption and contamination problems. Because of its low adsorptivity, we have decided to use 1-liter polycarbonate centrifuge bottles for environmental sampling.

Sample storage procedures must also be considered since immediate sample analysis is seldom possible. Preliminary studies in our laboratory have indicated that the room temperature shelf life of tributyltin in seawater solution stored in polycarbonate containers was 24-48 hours under laboratory lights. Since the tin-carbon bond is reasonably stable (Tobias, 1966), it appears that frozen storage under dark conditions in polycarbonate plastic containers might be the simplest and most effective approach for lengthy sample storage. Microbial activity would be minimized at subfreezing temperatures. Evidence for the degradation of TBTO to dibutyltin and monobutyltin derivatives by soil bacteria has been documented under laboratory conditions on growth media (Barug, 1981).

Tributyltin leachates from antifouling paint used as a toxicant source in bioassay studies conducted in our laboratory provided a reference sample source for frozen storage evaluation of sample stability. Previous analysis of tributyltin leachates in seawater from SPC-954 antifouling paint (International Paints, Inc.) had shown no monobutyl or dibutyltin species present in samples. We selected this leachate solution as an initial source for frozen storage evaluation. Several liters of seawater leachate solution were collected in a large plastic container and split into numerous aliquots contained in 500-ml polycarbonate plastic bottles. These samples were frozen and removed periodically for analysis. Results of frozen sample storage are presented in Table 6.

Table 6. Frozen storage and analysis of tributyltin in seawater.

Calendar Day	Tributyltin µg/liter
4/24/84	0.13
4/26/84	0.13
5/01/84	0.14
5/03/84	0.11
5/10/84	0.13
5/18/84	0.09
5/24/84	0.13
5/29/84	0.10
6/06/84	0.11
6/12/84	0.10
6/13/84	0.10
6/19/84	0.10
6/26/84	0.11
7/03/84	0.09
7/16/84	0.13
7/30/84	0.12
7/31/84	0.15
8/01/84	0.10

A mean value of 0.12 μg/liter tributyltin (STDV=0.02) was calculated for the 18 separate analytical determinations performed over the 100-day frozen storage period. The 95-percent confidence interval was calculated at 0.08-0.16 ppb. No detectable (detection limit = 0.006-0.009 μg/liter) monobutyl or dibutyltin was seen in the frozen samples analyzed. The results clearly indicate that freezing seawater samples containing tributyltin is an appropriate storage method. We have adopted frozen storage of samples as a method for maintaining a source of tributyltin reference samples to assure analytical accuracy in measurements.

D. Butlytins in Particulate and Dissolved Fractions of Marine Environmental Water Samples

A study was initiated to determine the amount of butyltin associated with the whole water and macroparticulate fractions of marine water samples collected in San Diego Bay. Association of butyltin species with particulate matter in the marine water column represents a transport pathway for deposition of butyltins in marine sediments via settling of the particulate matter. The relative amount of butyltin species present in the particulate fraction is, therefore, of interest in determining the environmental fate of butyltins. Reference to macroparticulate is that fraction removed by mild centrifugation, and the term is used synonymously with particulate.

Subsurface water samples were collected in 1-liter polycarbonate plastic bottles from Stations 2-1, 2-2, 2-3, 3-1, 3-2, and 3-3 (Figure 2). Samples from Stations 3-1, 3-2, and 3-3 were analyzed immediately after collection. Samples from Stations 2-1, 2-2, and 2-3 were analyzed 24 hours later. All analyses were performed by the HDAA method. Water samples were analyzed as the whole sample (noncentrifuged) and the particulate fraction (represented by the solid matter concentrated by centrifugation). The particulate fraction was resuspended in clean seawater prior to analysis. Samples were centrifuged for 10 minutes at 5000 rpm in 250-ml polycarbonate bottles.

Little, if any, butyltin species were detected in particulate matter separated from marine water samples by centrifugation. The data from six water samples collected from areas within San Diego Bay previously shown to contain butyltins are presented in Table 7. Butyltin concentrations measured in these particulate samples represented a minor percentage of the detectable butyltin in whole water samples. Data, therefore, indicate that the particulate fraction was not a significant source of butyltin in the environmental water samples analyzed. This conclusion is somewhat limited because very little particulate was separated from the whole water samples by centrifugation and consisted of relatively large particulate matter. Some question may exist regarding the ability of the hydride derivatization method to labilize butyltin species bound to particulate matter. Although the extent of the labilization may vary with the sample, Brinckman et al. (1981) have noted that the hydride derivatization method is a robust process and would be more likely to labilize particle-bound organotins than the high-performance liquid chromatography method.

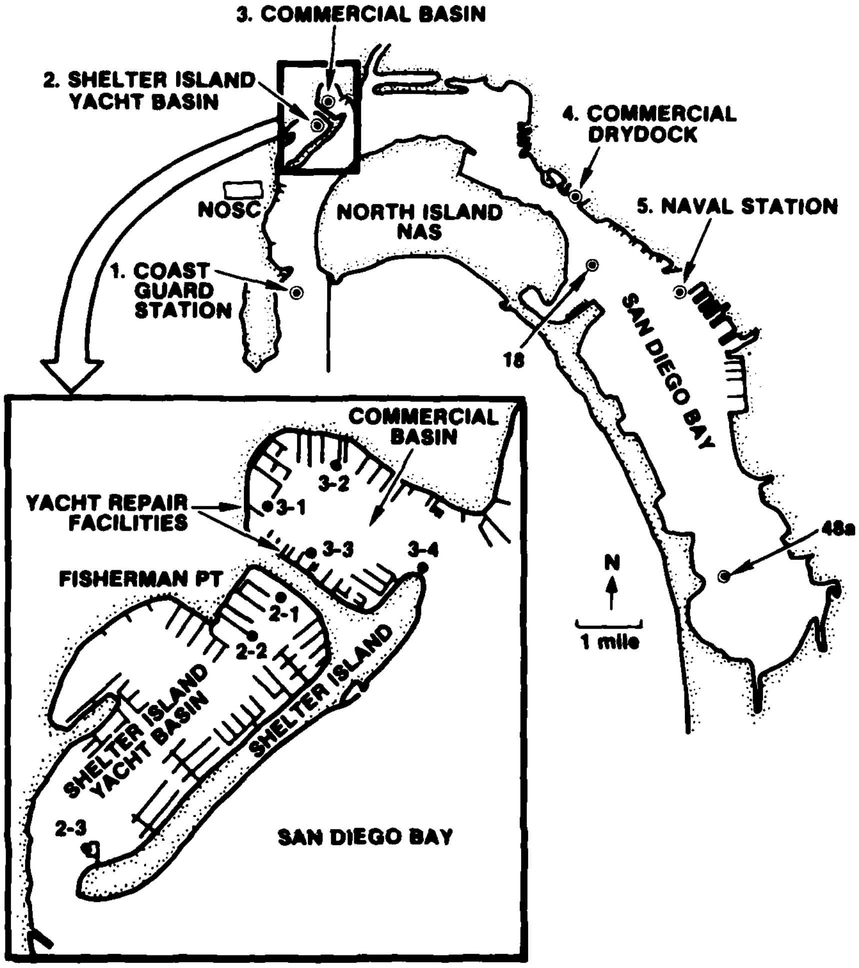


Figure 2. Sampling station locations within San Diego Bay.

E. Sulfide Interference to Sodium Borohydride Derivatization of Butyltins in Seawater and Natural Marine Sediments

The presence of sulfides in anoxic marine sediments is common and is known to occur in marine waters as well. The potential interference to borohydride reduction of butyltins by the presence of sulfides in seawater and sediments is of particular importance when determining the concentration of butyltin species in natural environmental samples. To assess potential sulfide interference to borohydride reduction, a standard solution mixture of monobutyltin, dibutyltin, and tributyltin was exposed to known amounts of sulfide just prior to reduction by sodium borohydride. Standards were exposed to known amounts of sulfide for 24 hours in polycarbonate bottles to test the effects of exposure for a longer period. Natural sediment containing known amounts of butyltins was also exposed to sulfide to test possible interference effects.

Table 7. Butlytin species detected in particulate and whole water samples.

	Monobutyltin (μg/L)	Dibutyltin (μg/L)	Tributyltin (μg/L)	Σbutyltin (μg/L)
Station 2-1				
Whole Water	NM	0.15	0.16	0.31
Particulate	ND	0.03	0.03	0.06
Station 2-2				
Whole Water	0.01	0.07	0.05	0.13
Particulate	ND	ND	ND	ND
Station 2-3				
Whole Water	0.06	0.05	0.09	0.20
Particulate	ND	0.01	0.01	0.02
Station 3-1				
Whole Water	ND	0.13	0.05	0.18
Particulate	ND	0.02	0.03	0.05
Station 3-2				
Whole Water	0.03	0.06	0.04	0.13
Particulate	ND	0.01	0.01	0.02
Station 3-3				
Whole Water	0.01	0.12	0.02	0.15
Particulate	ND	0.01	0.01	0.02

ND = no detectable signal
(detection limit = 0.01 μg/liter)

NM = peak was broad and poorly defined
(It was, therefore, not possible to determine the amount of monobutyltin present.)

A sulfide standard was prepared in nitrogen-purged distilled water by dissolving a known weight of sodium sulfide to a concentration of 2.5 times 10^{-2}M. Standard solutions of tributyltin (0.15 μg/liter), dibutyltin (0.16 μg/liter), and monobutyltin (0.11 μg/liter) were prepared in seawater and spiked with varying concentrations of standard sulfide solution. The final sulfide concentration in seawater solution ranged from 0.16 to 162 mg/liter.

The analytical sequence consisted of a 5-minute helium purge of the organotin standard solution, addition of the sulfide standard, a 2-minute mixing period without helium purging, and addition of sodium borohydride followed by a 5-minute reaction period where helium purging was resumed. Butyltin standards prepared in seawater and exposed to known concentrations of sulfide for 24 hours in 500-ml polycarbonate sampling bottles were analyzed by the same procedure. However, the 2-minute exposure interval to sulfide was omitted due to a longer 24-hour exposure period preceding it. Known weights of natural sediment (wet weight) from Station 3-1 (Figure 2) were analyzed by the same sequence used for standards in seawater with a 2-minute exposure to sulfide and no helium flow.

The solution pH was measured before and after sodium borohydride addition with all other reaction components present, including as much as 162 mg/liter sulfide. The pH values were 9.5 to 9.6, which are representative of solution pH values normally seen under our experimental conditions with seawater samples.

Analysis of monobutyltin, dibutyltin, and tributyltin species in seawater exposed to sulfide concentrations ranging from 0.16-162 mg/liter indicated that sulfide interference occurred at 162 mg/liter. Little or no interference expressed as a decrease in absorbance was seen at sulfide concentrations of 0.16-16.2 mg/liter (Table 8).

Table 8. Standard sulfide solution added to monobutyltin, dibutyltin, and tributyltin in seawater.

	Absorbance (In^2)		
	Monobutyltin 0.11 µg/l	Dibutyltin 0.16 µg/l	Tributyltin 0.15 µg/l
Standard-No Sulfide	0.47	0.71	0.52
Standard + 0.16 mg/l	0.51	0.66	0.43
Standard + 1.62 mg/l	0.38	0.69	0.54
Standard + 16.2 mg/l	0.30	0.65	0.46
Standard + 162 mg/l	0.09	0.27	0.02

The first experiment was essentially repeated, but with sulfide exposure lengthened to 24 hours prior to analysis. A control set of butyltins in seawater with no sulfide present was not used to test adsorption effects of container walls in this study since previous data had shown little or no change in the amount of butyltin measured in polycarbonate containers held at room temperature for 24 hours.

The results of the 24-hour exposure period to sulfide indicate that interference to borohydride reduction of dibutyltin and tributyltin may occur at 1.6 mg/liter sulfide when more exposure time is permitted. Monobutyltin hydride reduction apparently was relatively unaffected at sulfide concentrations of up to 16.2 mg/liter. Exposure to 48.6 mg/liter sulfide for 24 hours indicated that reduction of all three butyltin species was inhibited by sulfide (Table 9).

Table 9. Sulfide exposure to monobutyltin, dibutyltin, and tributyltin in seawater for 24 hours.

	Absorbance (In^2)		
	Monobutyltin 0.11 μg/l	Dibutyltin 0.16 μg/l	Tributyltin 0.15 μg/l
Standard-No Sulfide	0.23	0.83	0.62
Standard + 1.6 mg/l	0.32	0.67	0.32
Standard + 16.2 mg/l	0.26	0.37	0.16
Standard + 48.6 mg/l	0.08	0.45	0.16

An examination of the effect of sulfide on the sodium borohydride reduction of butyltins in natural marine sediment from San Diego Bay was also performed. Analysis of sediment from Station 3-1 had previously demonstrated the presence of all three butyltin species. After a 2-minute exposure period to 162 mg/l sulfide, borohydride reduction of monobutyltin, dibutyltin, and tributyltin was clearly inhibited. No absorbance was recorded for any of the three butyltin species. Some inhibition of tributyltin hydride formation was noted at 16.2 mg/liter sulfide (Table 10).

Table 10. Sulfide exposure to natural marine sediment from San Diego Bay.

	Absorbance (In^2)		
	Monobutyltin	Dibutyltin	Tributyltin
Sediment - No Sulfide (206 mg dry wt.)	0.20	0.60	0.53
Sediment + 1.62 mg/l (259 mg dry wt.)	0.20	0.63	0.47
Sediment + 16.2 mg/l (200 mg dry wt.)	0.28	0.50	0.22
Sediment + 162 mg/l (190 mg dry wt.)	ND	ND	ND

ND = no detectable signal

In summary, sulfide interference to borohydride reduction (hydride formation) of butyltins was noted at 162 mg/liter sulfide for all three butyltin species in seawater. After 24-hour exposures, interference was seen at 48.6 mg/liter sulfide for all three butyltin species. This indicates some dependence on exposure time, probably as a function of the sulfide-organotin reaction rate. Dibutyltin and tributyltin hydride formation was inhibited at 1.62-16.2 mg/liter sulfide after a 24-hour exposure. Sulfide interference to sodium borohydride reduction of natural marine sediments containing monobutyltin, dibutyltin, and tributyltin was evident at a 162-mg/liter sulfide exposure for a 2-minute period. None of the three butyltin species was detectable under the latter experimental condition. Tributyltin hydride formation in marine sediment was inhibited to a greater extent than monobutyltin or dibutyltin hydride formation. Exposure to 16.2 mg/liter sulfide for 2 minutes resulted in an approximate 50-percent decrease in tributyltin hydride formation.

The results of this study suggest that sulfide in the marine water column is not likely to interfere with butyltin detection by hydride reduction. However, highly anoxic marine sediments may contain sufficient concentrations of sulfide to cause an interference problem with the hydride formation method for butyltin detection and speciation.

To determine whether the formation of tributyltin sulfide derived from the presence of a sulfide anion might cause an analytical interference, a comparison of tributyltin calibration curves (using tributyltin chloride and sulfide compounds at equivalent amounts) ranging from 0.01-0.06 µg was performed to determine if either compound was more sensitive to borohydride reduction. A slope of 2.1 was determined for tributyltin chloride with an intercept of -0.002. Borohydride reduction of tributyltin sulfide gave a slope of 2.9 with an intercept of -0.0001. The 28-percent difference in the slopes of the calibration curves is near the analytical variability determined for analysis of tributyltin standards at 0.01 g amounts (Tables 1 and 2). No obvious difference in sensitivity to borohydride reduction was, therefore, determined.

Frozen tributyltin samples were also quantified by the method of standard additions. Both compounds were used to explore possible differences in the degree of borohydride reduction. Frozen seawater samples containing tributyltin (leached into solution from painted panels) were used as a sample set for analysis by standard additions with tributyltin chloride and sulfide. Frozen storage of tributyltin in seawater has proven to be a reliable method for sample preservation (Table 6). Previously, four samples from this set were analyzed on different days. The mean tributyltin concentration was 0.06 µg/liter with a standard deviation of 0.015. Determinations ranged from 0.04 to 0.08 µg/liter. The 95-percent confidence interval was calculated to be 0.03-0.09 µg/liter.

Three separate standard additions of tributyltin chloride to three samples from the reference set gave a standard addition curve with a slope of 2.7. The amount of tributyltin in the samples was determined as 0.03 µg/liter from the intercept on the x axis. An equal number of standard additions and amount of tributyltin sulfide to the reference samples gave a standard addition curve with a slope of 2.6. The amount of tributyltin in the samples was determined as 0.05 μg/liter from the x axis intercept. Both values were within the 95-percent confidence interval predicted for the reference sample set based on previous analysis. Again, no obvious differences in borohydride derivatization of either tributyltin compound were noted.

F. Hydrocarbon Interference to Sodium Borohydride Derivatization of Butyltins in Marine Water Samples

Attempts in our laboratory to quantify marine sediment samples (from areas where visible oil slicks were present) by standard additions alerted us to the possibility of hydrocarbon interference to borohydride derivatization of butyltins in samples containing fuel oils. Occasionally standard additions to marine sediment samples from such areas resulted in no detectable absorbance signals.

To determine if fuel oil could be directly responsible for the observed interference in hydride derivatization, we tested the effect of direct addition of diesel fuel to seawater samples containing tributyltin standard. Seawater samples spiked with 1 μg/liter tributyltin were analyzed by the HDAA method before and after diesel fuel was added directly to the reaction vessel where hydride formation takes place. The results indicated that diesel fuel at a concentration of 0.04 percent (400 ppm), or more, completely inhibited the formation of tributyltin hydride.

Possibly the presence of diesel fuel may act to partition tributyltin from solution (due to its Kow of approximately 6000 in seawater) and prevent formation of tributyltin hydride upon addition of sodium borohydride. Another possibility may exist. After butylin hydrides are formed, they must travel through a Teflon line from the reaction vessel to the quartz burner in our analytical system. The presence of diesel fuel in the reaction solution may result in some volatilization in the excurrent Teflon line. In this line diesel fuel may act as an adsorption surface for butyltin hydrides that pass by causing a loss of absorption signal in the detector. Other investigators have considered the possibility of butyltin hydride adsorption to internal surfaces and believe it is the most persistent difficulty with analysis of organotins by the hydride derivatization method (Andreae, 1981).

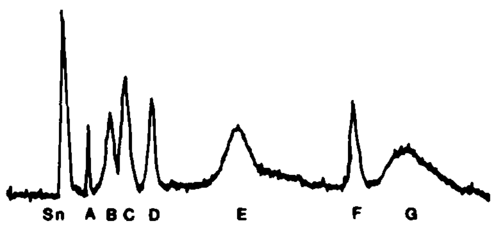
Certainly the loss of signal in analysis of complex environmental samples may present a problem where high levels of natural organics such as fulvic or humic acids or additive substances such as fuel oils may be present. Under such circumstances, accurate analysis of samples may necessitate the use of more than one analytical method capable of ultratrace detection and speciation of butyltins. We have not found organic interferences to be a significant problem in seawater analysis from a variety of harbors and estuaries.

G. Speciation of Mixed Butyltins and Methyltins in Seawater

Analysis of environmental samples in our laboratory occasionally resulted in the appearance of poorly resolved peaks between the inorganic and monobutyltin signals, particularly when quartz wool packing material was used in traps. These peaks may have been methyltin species. Several other investigators have detected methyltins and monobutyltin in fresh and saline water samples by hydride derivatization (Braman & Tompkins, 1979; Hodge et al., 1979; Jackson, et al., 1982; and Tugrul, et al., 1983).

To better define potential methyltin peaks in seawater samples, we modified the analytical procedure by adjusting the rate of heating to the trap where hydride species are collected prior to release to the detector. After hydrides were formed and collected in a trap packed with 3-percent OV1 Chromosorb, the trap was removed from the liquid nitrogen bath and held above it to permit a more gradual raise in temperature. Normally, the trap is removed, placed away from the liquid nitrogen bath, and allowed to come to room temperature.

Methyl and butyltin standards were added to organotin-free seawater and analyzed. The results are presented in Figure 3. With a more gradual heating rate, methyltins were released from the trap and resolved between the inorganic and monobutyltin peaks. Additionally, tetrabutyltin was resolved from tributyltin as a broad peak appearing after the trap was placed in heated (140°C) silicone oil. Serial additions of increasing amounts of tetrabutyltin standard resulted in an increase in peak area (Figure 4 A,B,C). The sharp peak appearing immediately after the trap was placed in oil, preceding tetrabutyltin in analysis where only tetrabutyltin was added, is attributed to tributyltin present as a degradation product of the tetrabutyltin standard. When increasing amounts of tributyltin and a constant amount of tetrabutyltin were added to seawater, this peak was notably enlarged (Figures 4D and 5D). Sample analysis without addition of $NaBH_4$ exhibited no peak preceding tetrabutyltin (Figure 5). This suggested that tributyltin was present in the tetrabutyltin standard. Analysis by GC methods confirmed the presence of tributyltin in the tetrabutyltin standard.



Sn = inorganic tin
A = 0.17 μg/liter monomethyltin
B = 0.12 μg/liter dimethyltin
C = 0.16 μg/liter trimethyltin
D = 0.12 μg/liter monobutyltin
E = 0.13 μg/liter dibutyltin
F = 0.10 μg/liter tributyltin
G = 1.00 μg/liter tetrabutyltin

Figure 3. Methyl and butyltin species detected by hydride derivatization in seawater.

The presence of an additional peak following tetrabutyltin in Figures 4 and 5 suggested that another contaminant was present in the standard. Or possibly, a redistribution product had formed as a consequence of the derivatization process. Sample analysis by GC methods, without borohydride derivatization, did not detect the presence of this additional peak. Possibly, the presence of this presumably larger molecular weight species was caused by the derivatization process in the presence of a relatively high tetrabutyltin concentration (1 ppb).

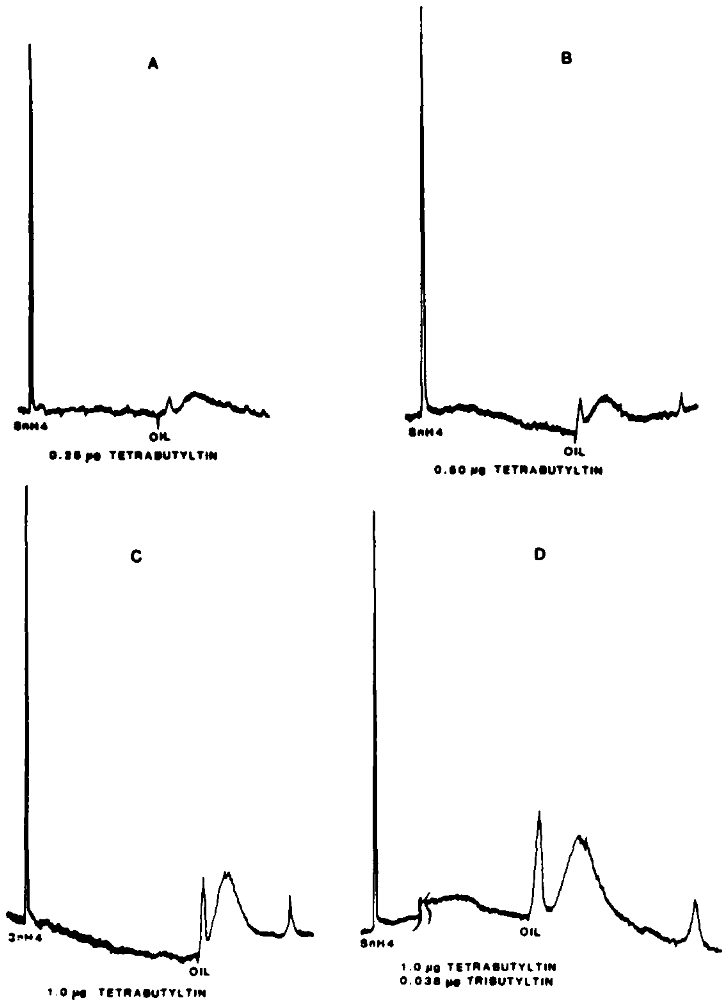


Figure 4. Determination of tetrabutyltin in seawater by hydride derivatization.

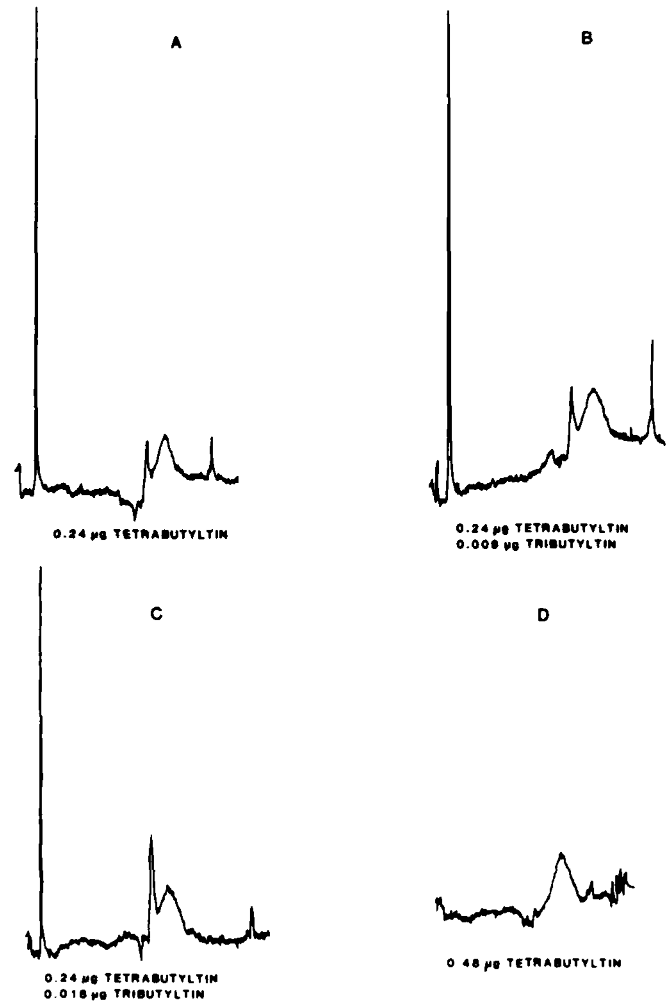


Figure 5. Determination of tributyltin and tetrabutyltin in seawater by hydride derivatization.

We have shown quantitative recovery of tributyltin in spiked standard solutions (Section B of this report). To confirm authentic speciation of tributyltin in environmental seawater samples, we compared the analytical results of sample analysis by gas chromatography-mass spectrometry (GC-MS) and the HDAA method. Tributyltin has recently been detected in environmental water samples at part-per-trillion (ppt) and in sediment samples at ppb concentrations by GC-FPD methods. Confirmation of authentic butyltin species was reported by GC-MS analysis (Mueller, 1984).

An environmental seawater sample from the Shelter Island Yacht Basin in San Diego Bay was analyzed by the HDAA method. A 1000-ml sample aliquot was then processed by the HDAA method. Rather than directing the tributyltin hydride to the atomic absorption detector, the excurrent line from the cryotrap was placed in 10 ml of hexane prior to immersion in the oil bath (Figure 6). The hexane fraction was analyzed by GC-MS.

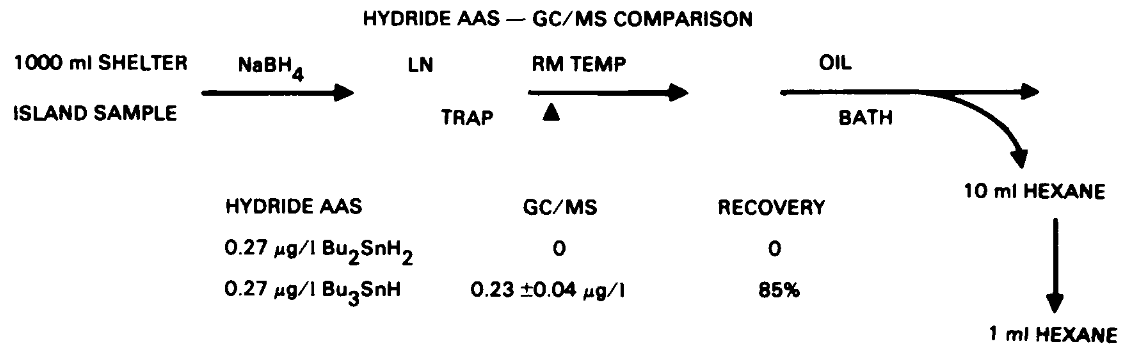


Figure 6. Gas chromatographic-mass spectroscopy confirmation of tributyltin in a natural seawater sample.

The results of GC-MS and HDAA analysis of sample aliquots were essentially identical. A tributyltin concentration of 0.27 μg/liter was determined by the HDAA method, while a 0.23 μg/liter tributyltin was determined by GC-MS analysis. There was an 85-percent agreement between the two methods. Dibutyltin was also detected by the HDAA method (0.27 μg/liter). Since this fraction is liberated from the cryotrap prior to immersion in the oil bath and was not collected for GC-MS analysis, a value is not reported (Figure 6). The results of this experiment demonstrated that in an environmental sample the fraction liberated from the cryotrap (upon immersion in hot oil) was composed of tributyltin hydride. The presence of tetrabutyltin in this fraction is possible, although we have shown that tetrabutyltin is detected slightly after tributyltin (Figure 4D). Diphenyltin has been reported to be released nonquantitatively upon heating the cryotrap (Hodge et al., 1979). Since diphenyltin is a degradation product of triphenyltin, a pesticide, its presence in marine environmental samples is unlikely in areas where little or no agricultural runoff occurs.

H. Analysis of Butyltins in Seawater by the Method of Standard Additions

Analysis of environmental samples for ultratrace levels of organometallic compounds, such as butyltins, may be quite problematic in areas where diverse natural and anthropogenic inputs of organic materials exist. Specifically, release of such substances as fuel oils and complex textile mill effluents may contribute to analytical difficulties. To address the existence of positive or negative analytical interferences in natural environmental samples, the method of standard additions should be routinely employed. This is especially true in areas that have not been well studied. If significant analytical interferences are not detected, sample analysis may proceed by routine calibration with known amounts of pure standard. Unknown amounts of butyltins in environmental samples may then be determined by calculation from calibration curves.

Our laboratory analysis of seawater samples (from various marine harbors) has generally documented few analytical interferences with borohydride derivatization of butyltins. We chose to compare results from samples analyzed from enclosed yacht harbors and those collected from open harbor sites to further investigate possible matrix interferences in butyltin analysis with natural seawater samples. The yacht harbor sites represent areas where relatively little water circulation is possible and maximum input of fuels and other pollutants was anticipated. Samples collected in open harbor sites were considered representative of relatively clean water. These samples were essentially free of substances encountered in much higher concentration in the yacht harbors. Samples collected for this comparison were taken from Shelter Island Yacht Harbor, the Commercial Basin, and from south San Diego Bay (Figure 2). The results of triplicate analysis of water samples by calibration curve calculation and by the method of standard additions are presented in Table 11. Three standard additions were made to each of three replicate samples collected in the yacht harbors. Samples collected in south San Diego Bay were collected in 8-liter polycarbonate bottles and analyzed as a single sample by calibration curve calculation and by standard additions.

Generally, the results of analysis of seawater samples collected in yacht harbors compared well by both methods. Mean values determined for replicate analysis of dibutyltin and tributyltin species and 95-percent confidence limits calculated for both methods were similar. A 50-percent difference in the amount of dibutyltin detected in samples collected in the Commercial Basin represented the largest difference noted. Both concentrations were low (0.04 and 0.02 µg/liter, respectively) representing a very small amount of dibutyltin. The largest difference in the amount of tributyltin (determined by both quantification methods) in yacht harbor samples was 29 percent. These samples were collected from Station 2-1. In the yacht harbor samples analyzed, monobutyltin was not present above detection limits (0.005 µg/liter). Concentrations of dibutyltin and tributyltin (calculated by both methods) compared well in water samples collected from open bay areas (Stations SD-18 and SD-48a). Monobutyltin was present at levels near the detection limit (0.005 µg/liter) in open bay samples and was not quantified.

Table 11. A comparison of butyltin species concentrations determined in seawater samples by calibration curve calculation and by standard additions.

	Station Yacht Harbor	Dibutyltin (µg/liter)	Tributyltin (µg/liter)
Calibration Curve Determination	2-1 Rep. 1	0.16	0.32
	2-1 Rep. 2	0.23	0.31
	2-1 Rep. 2	0.19	0.26
	2-1 Rep. 3	0.16	0.25
	$\bar{X}$ =	0.185	0.285
	STDV =	0.029	0.030
	CV =	15.7%	10.5%
	95% Confidence Limit =	0.13-0.24	0.23-0.35
Standard Addition	2-1 Rep. 1	0.21	0.23
	2-1 Rep. 2	0.27	0.22
	2-2 Rep. 3	0.16	0.16
	$\bar{X}$ =	0.213	0.203
	STDV =	0.045	0.031
	CV =	21.1%	15.3%
	95% Confidence Limit =	0.12-0.30	0.14-0.27
Calibration Curve Determination	3-1 Rep. 1	0.04	0.08
	3-1 Rep. 2	0.05	0.09
	3-1 Rep. 3	0.03	0.11
	$\bar{X}$ =	0.04	0.09
	STDV =	0.01	0.015
	CV =	25.0%	17.0%
	95% Confidence Limit =	0.02-0.06	0.06-0.12
Standard Addition	3-1 Rep. 1	0.03	0.07
	3-1 Rep. 2	0.02	0.13
	3-1 Rep. 3	0.01	0.12
	$\bar{X}$ =	0.02	0.11
	STDV =	0.01	0.03
	CV =	50.0%	27.3%
	95% Confidence Limit =	0.00-0.04	0.05-0.17
	Open Bay	**Dibutyltin**	**Tributyltin**
Calibration Curve	SD-18	0.020	0.018
	SD-48a	0.030	0.028
Standard Addition	SD-18	0.034	0.024
	SD-48a	0.033	0.028

The results suggest that small analytical interferences may be present in areas such as yacht harbors. The degree of interference, relative to the amount of butyltin species present, represents a rather small proportion of butyltin species quantified. Conditions may possibly exist in other areas where more severe analytical interferences may be encountered. In lieu of effective sample pretreatment procedures, where interfering compounds may be removed prior to analysis without loss of butyltins, some assessment must be made of potential analytical interferences. A comparison of calibration curve calculations and standard addition results could accomplish this assessment.

I. Sediment Analysis Data

The hydride derivatization method has been evaluated in our laboratory to analyze butyltins in marine sediments. Weighted sediment aliquots are placed in the reaction vessel and the dead space is filled with seawater. The analytical sequence is identical to that described in the methods and materials section of this report. Sediments are mechanically homogenized and aliquots are removed for analysis. Generally, sample aliquots of 0.5 gm or less are sufficient for detectable signals from sites where butyltins are measured in the water column. Results may be calculated in terms of sediment dry weight by removing a wet aliquot and drying the sample for 24 hours in an oven at the desired temperature. A wet/dry weight ratio may be calculated and used to convert wet weight data to dry weight.

The results of replicate analysis of four sediment aliquots from a single sediment sample (collected from Station 2-3 located in an area of dense yacht activity) are reported in Table 12. The data are expressed in µg/kg.

Table 12. Replicate analysis of Station 2-3 sediment from San Diego Bay.

	Monobutyltin	Dibutyltin	Tributyltin
Replicate 1	65.2	16.0	26.7
Replicate 2	27.4	15.5	26.0
Replicate 3	27.5	12.8	35.9
Replicate 4	33.1	21.4	20.4
$\bar{x}$	38.3	16.4	27.3
STDV	18.1	3.6	6.4
Coefficient of Variation	47.3%	22.0%	23.5%

The results indicate that direct analysis of marine sediments by the HDAA method is similar in relative precision to direct analysis of seawater. The coefficient of variation calculated for monobutyltin was considerably larger than those calculated for dibutyltin and tributyltin. A single large value determined in the first replicate accounted for the higher standard deviation seen in the monobutyltin data. There is an increased possibility of nonhomogeneous samples presented by sediments, where various degrees of particle association with butyltins might occur. The data generated for direct analysis of marine sediment after sample homogenization indicate that the procedure is comparable to direct analysis of seawater with respect to precision. A number of core samples have been collected and analyzed for butyltin content from several stations in San Diego Bay and are reported separately (Stang, 1985).

A comparison of quantitative analytical results by calibration curve determinations and the method of standard additions was performed with marine sediment samples collected in San Diego Bay at Stations 2-2 and 2-3 during January 1983 (Figure 2). The samples were homogenized and frozen prior to analysis. Core samples were taken from the frozen homogenates with plastic tubes and used directly for analysis. The results are presented in Table 13 as µg/kg wet weight.

Table 13. Analysis of marine sediments from San Diego Bay (µg/kg/wet weight).

Station	Monobutyltin	Dibutyltin	Tributyltin	Total
2-2				
Calibration Curve	31.8	28.0	46.0	105.8
Standard Addition	45.7	7.4	119.9	173.0
2-3				
Calibration Curve	10.6	55.7	22.6	88.9
Standard Addition	7.2	8.6	67.5	88.3

Generally, little agreement was found in the concentration of a particular butyltin species determined by either method of quantification. Monobutyltin values were the most comparable. Less dibutyltin and more tributyltin were determined in samples quantified by the method of standard additions. The results suggest that marine sediment samples may be quite variable in butyltin content. Speciation of butyltins may be dependent on sample matrix composition, as indicated by variable butyltin concentrations determined by calibration curve and standard addition quantification methods. Due to the possibility that such matrix components of marine sediments, as hydrocarbons and sulfides, may exist in high concentrations and interfere with borohydride reduction of butyltins directly, the technique may be most useful under experimental conditions where the sediment has demonstrated a low matrix interference.

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ABBREVIATIONS AND SYMBOLS

AAS	Atomic absorption spectroscopy
$BnSnH_3$	Butyltin trihydride
Bu_2SnH_2	Dibutyltin dihydride
Bu_3SnH	Tributyltin hydride
cc	Cubic centimeter
cm	Centimeters
CPVC	Chlorinated polyvinylchloride
CV	Coefficient of variation
°C	Degrees Celsius
ETOH	Ethanol
GC-MS	Gas chromatography-mass spectrometry
GFAA	Graphite furnace atomic absorption
gm	Gram
HCL	Hydrochloric acid
HDAA	Hydride derivatization atomic absorption
HNO_3	Nitric acid
ID	Inner diameter
In^2	Inches squared
Kow	Octanol-water partition coefficient
L	Liter
M	Molarity
ma	Milliamperes
mg	Milligram
mg/kg	Milligram per kilogram
MIBK	Methyl isobutylketone
min	Minute
ml	Milliliter
mm	Millimeters
mv	Millivolts
μ	Micron
μg	Microgram
μg/kg	Microgram per kilogram
N	Normality
N_2	Nitrogen
$NaBH_4$	Sodium borohydride
NaOH	Sodium hydroxide
NBS	National Bureau of Standards
nm	Nanometers
OD	Outer diameter
pH	Hydrogen ion concentration
ppb	Parts per billion
ppm	Parts per million
ppt	Parts per trillion
PVC	Polyvinylchloride
rpm	Revolutions per minute

ABBREVIATIONS AND SYMBOLS (Continued)

Sn	Tin
SnH_4	Tin (IV) hydride (Stannane)
STDV or S	Standard deviation
TBTCl	Tributyltin chloride
TBTO	Bis(tri-n-butyltin) oxide
$\bar{X}$	Mean
<	Less than

APPENDIX A

ANALYTICAL PROCEDURE FOR DETERMINATION OF BUTYLTIN COMPOUNDS IN SEAWATER: METHODS AND MATERIALS

Procedure modified from V.F. Hodge, S.L. Seidel, and E.D. Goldberg (1979) Anal. Chem., 51:1256.

1. **EQUIPMENT**

A. Atomic Absorption Spectrophotometer (AAS) with tin lamp

B. Recorder - set chart speed at 2 cm/min; run on 50 mv

C. Quartz burner (see Figure A-1) (Figures appears on pages A-9 to A-11.)

(1) Adaptor mount (see Figure A-2)

D. Gas washing bottle - adapted as per diagram

E. F.E.P. Teflon tubing/glass U trap

(1) Teflon reducer fittings and 1/4-inch straight fitting

F. Silicone oil - high temp (400 °C) + 0-220 °C thermometer

G. Magnetic stirrer, hot plate, Teflon coated stirring bar

H. Ringstand with several clamps

I. Liquid nitrogen source and small (1-liter container) dewar

J. Tygon tubing 1/4-inch for gas lines

K. Helium, air, hydrogen gas cylinders with regulators

L. In-line gas control valves

M. 5-cc syringes - plastic disposable
(1) 2-inch steel needles, 22 gauge

N. Filter paper (Whatman #1 or 2)

O. Volumetric glass flasks with ground glass fits 100 ml/50 ml

P. 500-ml gas washing bottle (see Figure A-3) with 34/28 tapered glass fit

Q. Asbestos strip approximately 1/2-inch wide for mounting quartz burner in aluminum furnace adaptor mount

2. **CHEMICALS**

A. Sodium borohydride

B. Sodium hydroxide

C. 95-percent Ethanol

D. Tributyltin chloride (or bis(tri-n-butyltin) oxide)

E. Dibutyltin dichloride

F. Monobutyltin trichloride

G. Ultrex acetic acid

H. Atomic absorption inorganic tin standard

I. Clean seawater free of organotins - necessary to find a reference area where such water is available - keep in glass container

J. RBS-35 soap

3. F.E.P. TEFLON CARRIER GAS LINES AND GLASS U TRAP

A. The carrier lines should be made of F.E.P. Teflon, which is very non-absorptive.

(1) We use 1/8-inch OD tubing.

(2) The length of the lines should be minimized to avoid excess condensation surface for water vapor.

(3) Incurrent and excurrent lines used in this laboratory are 17 inches long, but may be modified by arrangement of the gas washing bottle, magnetic stirrer, ringstand, and oil bath system.

B. A glass U-trap 2-1/2 inches long at either arm is used to trap the hydrides.

(1) We use capillary glass tubing approximately 2-mm ID bore packed with quartz wool (recently 3-percent OV1 Cromosorb approximately 1 gm has worked best).

(2) Packing should be slightly compact; very tight packings seem to give poor peak definitions.

(3) The glass U-trap should be ground down at the ends to reduce the diameter and permit a tight fit into the 1/4-inch to 1/8-inch Teflon reducer fittings placed on both ends.

(4) The F.E.P. Teflon tubing must be sanded down to fit tightly into the glass U-trap (3/4-inch in depth).

C. A diagram of the system with all equipment components identified is shown in Figure A-4.

4. ANALYTICAL PROCEDURE

A. Equipment Setup and Check

(1) Turn on power to AA and warm up lamp. Lamp to quartz burner alignment should be optimized daily. Warm up 30 minutes.

(2) Proper wavelength setting should be optimized daily (286.3 nm).

(3) Gas flows should be set at 220/140/40 ml/min with respect to hydrogen/air/helium.

- If the flame is not hydrogen rich, tin detection may not occur.

- The flame should be checked often at both ends of the burner, as it may occasionally go out.

(4) Silicone oil heated to 140-160 °C.

(5) Liquid nitrogen dewar maintained filled.

B. Reagent Preparation

(1) Filter a 4-percent sodium borohydride solution made in 1-percent sodium hydroxide/distilled water solution.

(2) Make up a 2N acetic acid solution in distilled water.

(3) Make primary standards of tributyltin, dibutyltin, and monobutyltin in 95-percent ethanol at 100-150 ppm concentrations in 50-ml volumetric flasks - these standards may be made at higher concentrations, but we find these to be convenient for dilution to working standards - a shelf life of 2 days is recommended.

(4) Make working secondary standards in a range 1-1.5 ppm by dilution of the primary standards in 95-percent ethanol. A shelf life of 2 days is recommended.

C. Analysis Sequence

(1) Establish an acceptable blank with clean organotin-free seawater.

- A reagent blank should be determined if inorganic tin (IV) is to be quantified.

(2) Construct a calibration curve for all three butyltin species as well as inorganic tin. These tin species may all be quantified in a single analysis.

- If only a single species is of interest, the others need not be introduced into the reaction mixture.

(3) We find that pipetting working standards directly into a 500-ml seawater volume in the gas washing bottle with Eppendorf pipettes is practical and sufficiently accurate.

(4) We find that a calibration curve with a range of 0.01-0.10 μg of each of the butyltin species is practical with three calibration points.

- Inorganic tin may be measured at lower levels (possibly to 0.001/μg).

(5) Run a seawater blank through the system after the calibration curve is completed. Some carryover of hydride compounds may be encountered, especially after a run with as much as 0.1 μg tributyltin present.

(6) Analysis of samples may now proceed. Generally, environmental seawater samples require a 500-ml sample for a detectable signal.

(7) A standard point from the calibration curve should be repeated at least every fifth run to evaluate the condition of the system and normalize peak areas if necessary.

D. Sample Analysis

(1) A 500-ml sample is placed in the gas washing bottle reaction vessel and acidified with 2N acetic acid (500 ul 2N acetic acid/500 ml sample).

NOTE: If a sample is less than 500 ml, enough clean seawater should be added to make the final volume 500 ml. This is to prevent dead space in the reaction vessel, which attenuates the signal by adsorbing volatile hydrides.

(2) The U-trap is placed in liquid nitrogen.

- The trap should be submerged in liquid N_2 just enough so the column packing is covered.
- Too much submergence may cause water vapor to freeze and form an ice block. Occasionally this may happen anyway resulting in back pressure to the reaction vessel and loss of the sample through escaping gas.

(3) After the trap is submerged for approximately 1 minute, 4-percent sodium borohydride is injected through a port in the reaction vessel - 5-cc borohydride/500-ml seawater sample.

- The sample is allowed to mix with the borohydride for 5 minutes, during which time the hydrides formed are carried into the glass U-tube and trapped.

(4) Separation of the inorganic tin (IV) and butyltin species is accomplished by removing the trap from the liquid N_2 and allowing it to come to room temperature. Tributyltin hydride is released by placing the U-trap in the hot (140 °C) silicone oil. Separation is in the order inorganic tin (IV), monobutyltin, dibutyltin, and tributyltin.

- The trap is left in hot oil for 10 minutes to drive off excess water vapor introduced by the carrier gas.

(5) Detection occurs in the quartz burner with consequent recording of peak areas. Quantification is accomplished by peak integration.

- Sample peaks are compared with authentic standard retentions to confirm species.

(6) The reaction vessel is emptied and rinsed with distilled water prior to analysis of another sample. The stem of the gas washing bottle is also rinsed.

5. POTENTIAL PROBLEMS

A. No signal from a standard or sample - repeat run - if no signal:

(1) Check instrument parameters, flame, and especially gas flow rates.

(2) It may be necessary to remake the borohydride if an error was made.

(3) It may be necessary to remake the standards especially if they were kept in excess of 2-4 days.

B. No signal or poor signals, poor linearity, possibly loss of tributyltin signal. System may have experienced some buildup of volatile substances.

(1) The condition of the Teflon lines and trap seems to change with time and the number and nature of samples run through the system. Repetition of standards is necessary to aid in evaluating the system. Approximately every 10 working days we change the Teflon lines and clean the trap by removing the packing material, cleaning the glass with acetone, and repacking the trap. This is easier than attempting to clean the lines. We are currently preparing to test the use of silanized glass, lines, and the U-trap after recommendations made by Andreae in a recent publication. Hopefully this will improve the service life of the system. Occasionally, the tip of the Teflon line entering the quartz burner may burn, resulting in a loss of signal. It should be positioned at least 1/2-3/4 inches from the main cylinder body of the quartz burner.

MAJOR EQUIPMENT ITEMS

NOTE: The U.S. Navy does not endorse specific products; these are presented for information only. Similar products from other sources are available.

1. Atomic Absorption Spectrometer, Buck Scientific Model 200, with adapter for 1-1/2 and 2-inch lamps.

   - Available from Western Analytical Products Co., Inc.
     4502 Lakeview Avenue
     Yorba Linda, CA 92696
     (714) 558-7300

2. Linear Instruments Corp. Model 585 Flat Bed Recorder with 2 inputs, 22 chart speeds/programmable, 12 input spans, 1mV-5V, servo kill feature.

   - Available: same as in 1.

3. Quartz Burner - should be fabricated by glass blower - local availability should be possible - see attached plans (Figure A-1) (same for gas washing bottle modifications, Figure A-3).

4. Burner mount for quartz burner - fabricated by machine shop. Local availability should be possible. See attached plans (Figure A-2). The existing flame burner head in the atomic absorption spectrophotometer may be used to seat the quartz burner if it is a flat surface. The burner may be clamped to the burner head and, thus, the position of the entire assembly may be adjusted with the instrument controls. We have constructed a burner seat assembly for our Buck AA and have provided a copy of plans.

5. Teflon tubing and connectors:

   - Available Fluoroware, Inc.
     Jonathan Industrial Center
     Chaska, MN 55318
     (612) 448-3131

     (1) F.E.P. tubing - OD 1/8 = 0.125", ID 1/16 = 0.062", Cat. #ET125-030, 100 ft.

     (2) Grooving tool for 1/8" tubing, Cat #GT2.

     (3) Straight Union Reducer, 1/4" and 1/8", Cat. #Su4-2N FN4. FN2 nuts included; need 6.

     Straight Union 1/4", Cat. #SU2N, need 1.

6. Chemicals:

- Organotin standards - available Pfaltz and Bauer Chemicals or Ventron Chemicals.

- Sodium Borohydride - carried by most suppliers - distributed by Kodak.

- 95-percent Ethanol - this is not denatured - available U.S. Industrial Chemicals.

- Others chemicals are generally available through most suppliers.

7. Miscellaneous Equipment Items

- Gas washing bottle - type with 34/28 tapered glass fitting, 500 ml.

- Other items are general supplies and should be available through most lab suppliers.

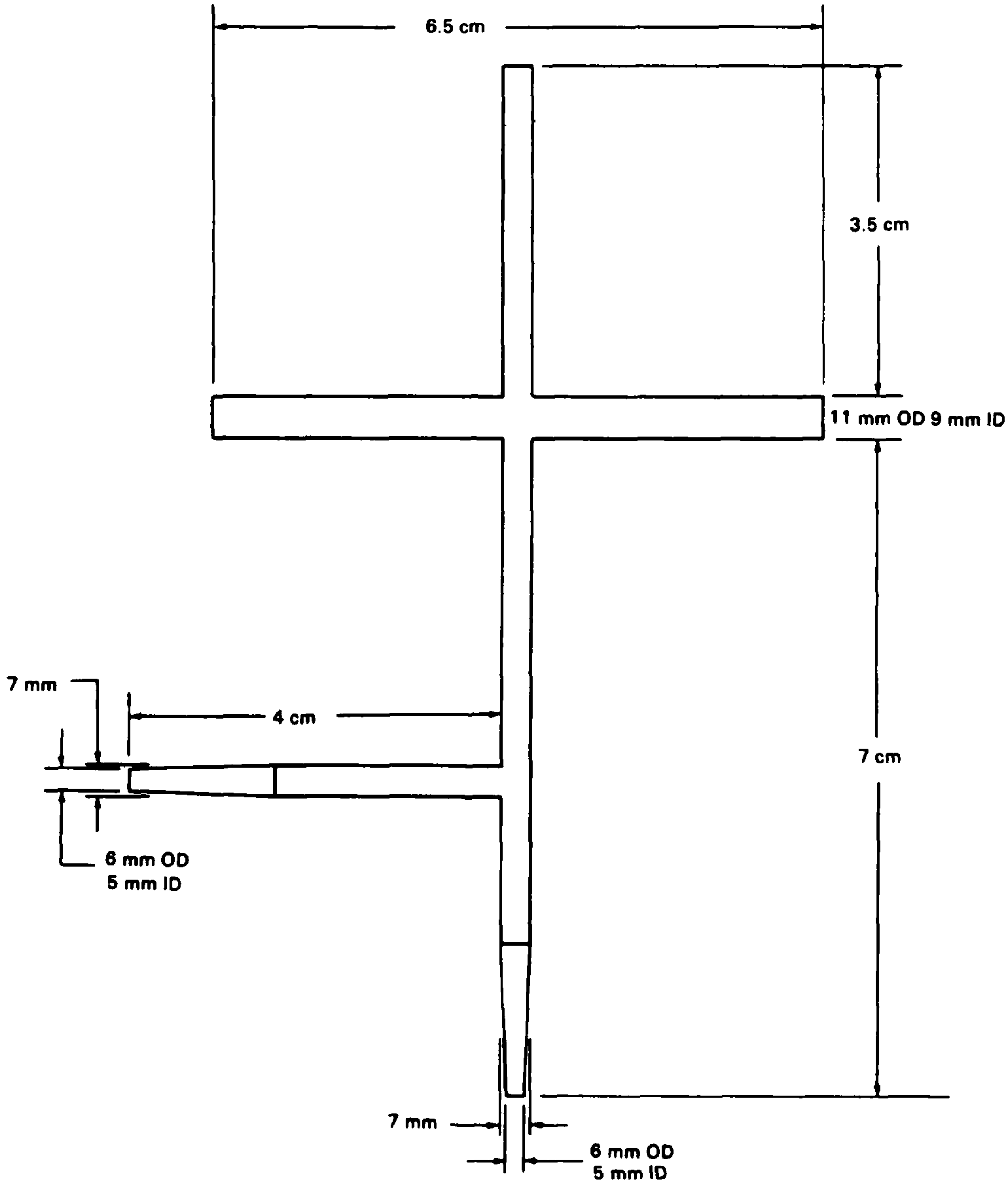

Figure A-1. Quartz burner specifications.

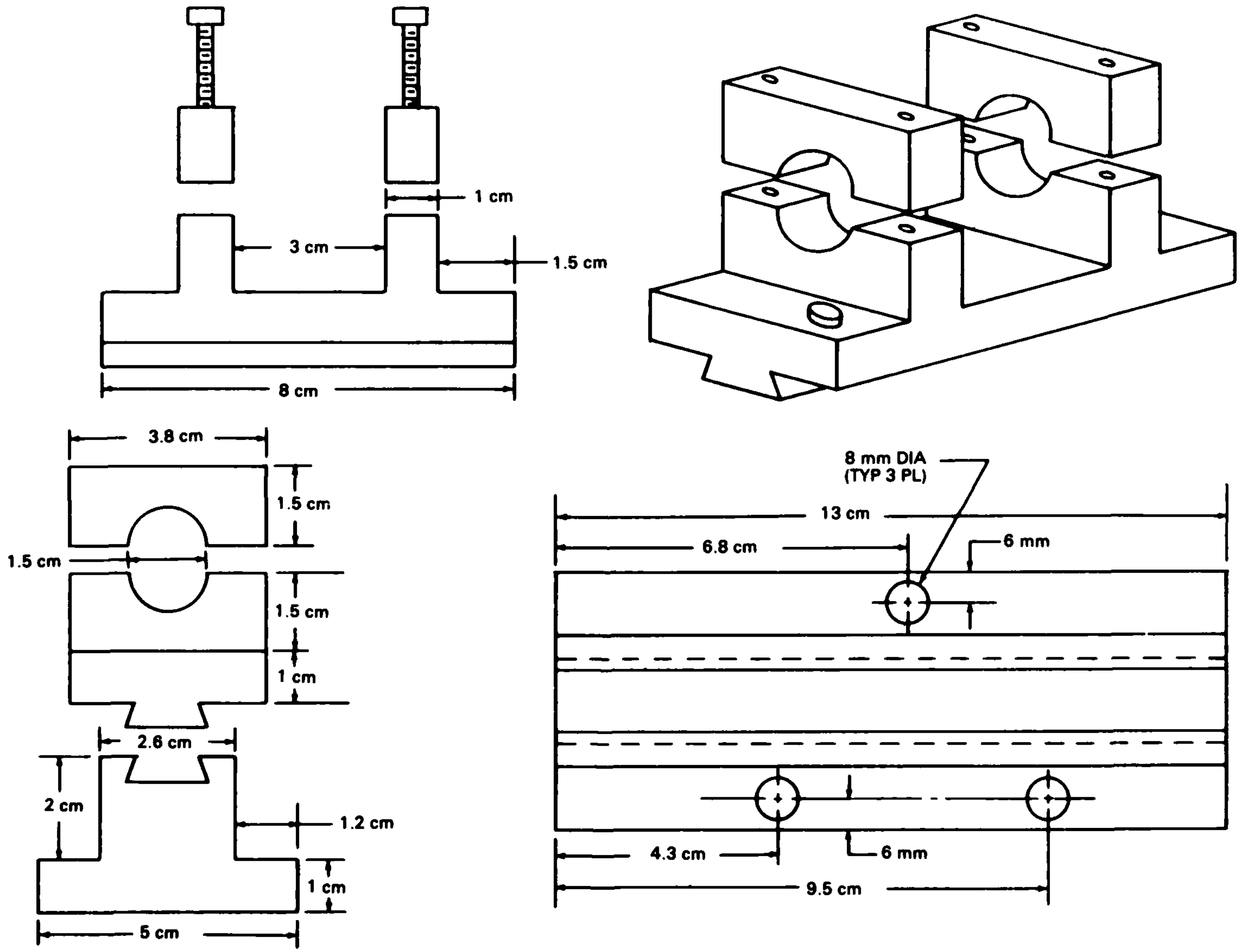

Figure A-2. Quartz furnace adaptor mount.

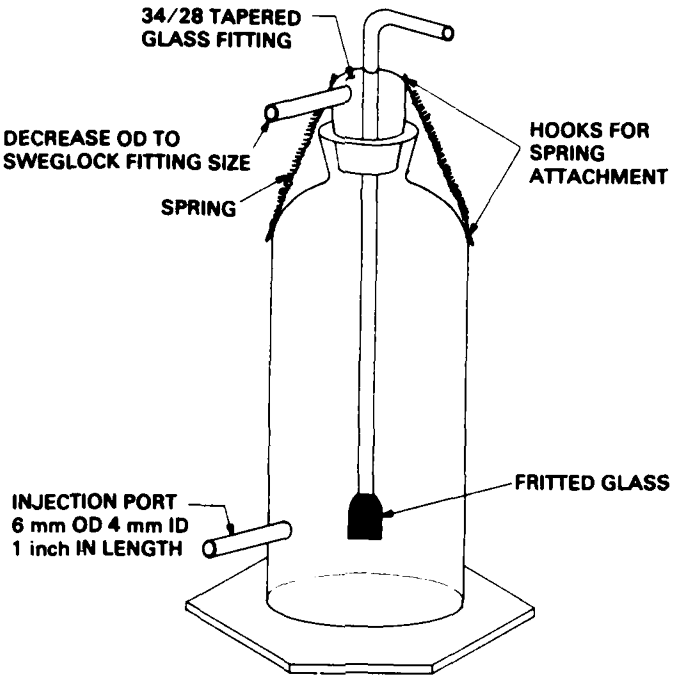

Figure A-3. Modifications to gas washing bottle.

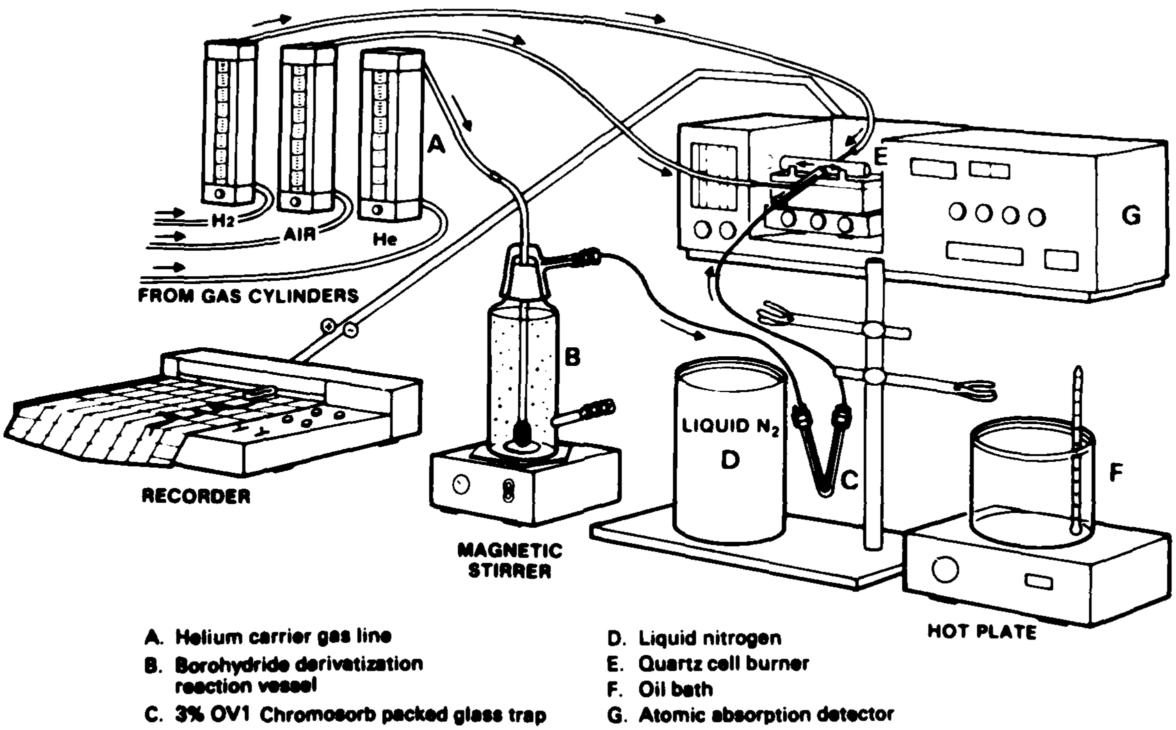

Figure A-4. Hydride generation/atomic absorption spectrophotometry system for measurement of organotin species.

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